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The impact of fertilization and hydrology on nitrate fluxes from Mississippi watersheds

Peter A Raymond[1], Mark B David[2] and James E Saiers[1]

The watersheds of the Mississippi are some of the most intensively managed agricultural basins in the world. As such, they receive high loadings of nitrogen and export a large amount of nitrate to the drainage networks of the Mississippi River basin and coastal ocean. We find a positive correlation between fertilizer input and stream export of nitrogen. According to the correlation, ~34% of applied fertilizer nitrogen is exported to streams and rivers of the Mississippi basin, a fraction that is greater than the global average. The relationship is partly causal, but also reflects indirect effects, as fertilizer application in the Mississippi basin also correlates with agricultural practices, such as row cropping and tile drainage. The overall impact of these agricultural practices is to increase water throughput and decrease water and nitrogen residence time and processing, which, in turn, increase nitrogen export and the percentage of fertilizer that is exported. This response, coupled with a general increase in precipitation in the Mid-West, is exacerbating the nitrogen problem and will decrease the efficacy of nitrogen-reduction management.

Addresses
[1] Yale School of Forestry and Environmental Studies, New Haven, CT, United States
[2] University of Illinois, Department of Natural Resources and Environmental Sciences, Urbana, IL, United States

Corresponding author: Raymond, Peter A (peter.raymond@yale.edu)

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Introduction

The fluvial export of terrestrial nutrients impacts downstream ecosystems [1,2]. The export has been exacerbated by anthropogenic activities that have increased the import of limiting nutrients into watersheds [3]. At the watershed scale, these imports include atmospheric deposition, food and feed, fertilizers, and waste-water [4]. In the United States, the inputs of nitrogen from human activities have roughly doubled in the 20th century [5,6] and now many watersheds receive loadings that are many times that of pre-anthropogenic inputs. A secondary driver of changes in element delivery to coastal systems is alterations in the hydrology of upstream watersheds [7•,8]. These changes can be due to climatic and/or land management changes and can interact with nutrient inputs to alter fluxes.

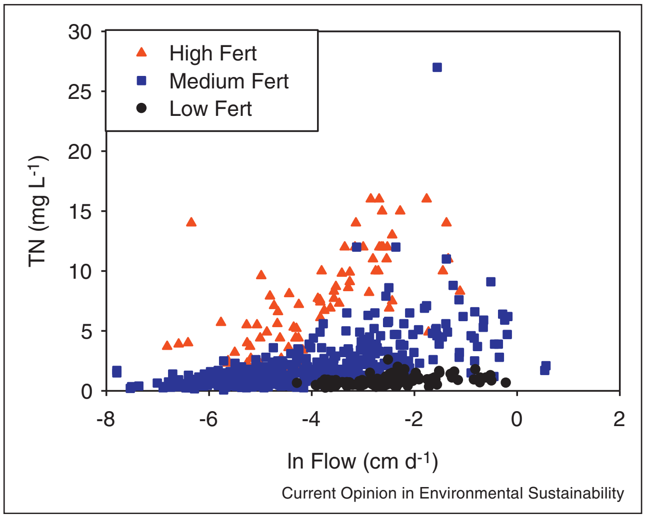
The large increase in nutrient loading has led to the impairment of many water bodies globally [9]. This includes the eutrophication of water bodies that can lead to dissolved-oxygen depletion, species shifts, and fish kills [1]. Recently it has also been suggested that nitrate concentrations in agricultural streams correlate with a significant outgassing of the greenhouse gas N_2O [10•]. The main management tools to alleviate eutrophication involve reducing nutrient imports into watersheds or to develop green and grey infrastructures that increase nutrient processing and removal within watersheds [11]. The relative efficacy of these management approaches is highly dependent on the biophysical response of the watershed to the type and timing of nutrient loading and the overall hydrologic conditions. The purpose of this paper is to provide a brief review on the importance of fertilizer inputs to the overall export of nitrogen from the Mississippi River basin, with an emphasis on the impact of watershed hydrology on the riverine export of nutrients derived from fertilizer application.

Fertilizer and watershed nitrogen export

In agricultural soils, nitrate is typically the dominant form of N and is highly mobile [12]. In the Mississippi River, nitrate concentrations have increased by ~2.5, accounting for almost all the increase in nitrogen flux [13,14]. For the Mississippi River watershed, annual flow and net anthropogenic nitrogen inputs (NANI) was highly correlated with annual riverine nitrate flux for the periods post 1960–1996 [15]. This temporal statistical relationship was driven mainly by the tight correlation between flow and flux and the almost doubling of fertilizer input over this time frame. The long term change in nitrogen loading has been linked to an intensification of hypoxia in the Gulf of Mexico [16].

The within watershed dynamics of the Mississippi provide interesting insights into the importance of fertilizer on total nitrogen (TN; nitrate, nitrite, ammonia, dissolved organic nitrogen, particulate organic nitrogen) export. Across watersheds of the Mississippi, the amount of nitrogen exported during hydrologic events increases with the amount of fertilizer applied (Figure 1 [17••]). The rating curves (Figure 1) of subwatersheds with a

Figure 1



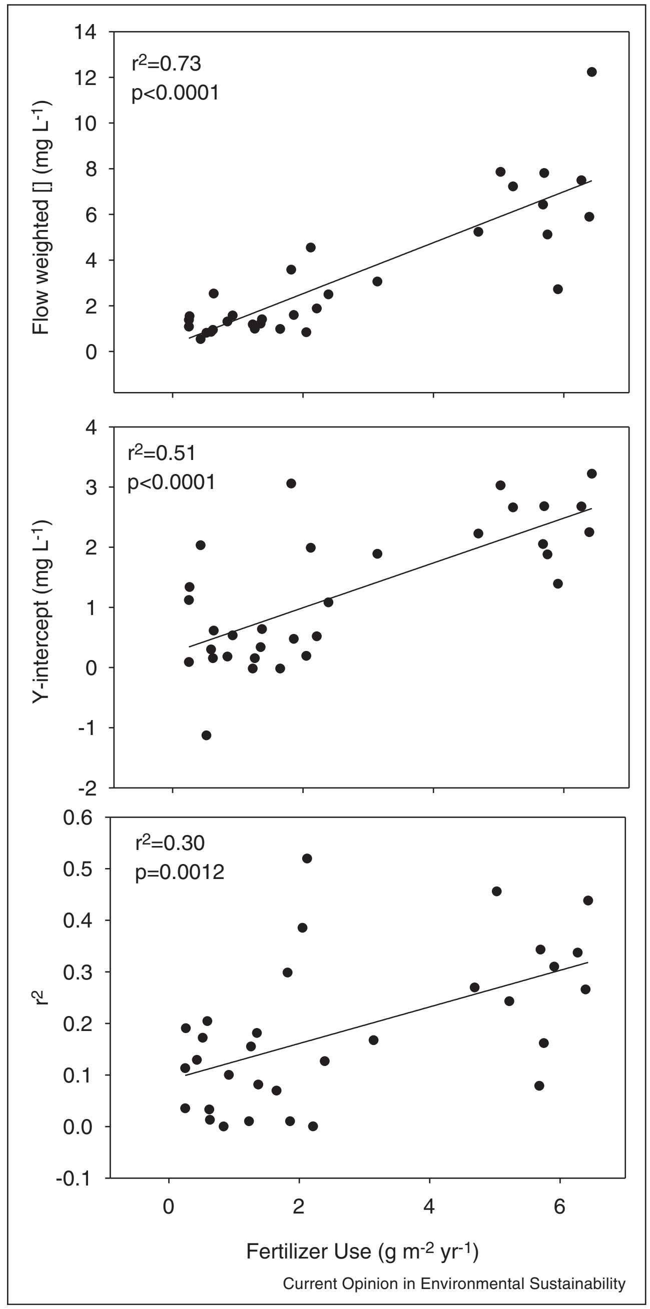
Rating curves for high, medium and low fertilizer use watersheds. The high, medium and low fertilizer watersheds are the Raccoon River IA, Grand River MO, and St. Croix River WI, respectively.

higher loading of fertilizers have a higher r^2, y-intercept and flow weighted annual concentration (Figure 2). This is consistent with the rapid delivery of nitrate to streams and rivers in these highly managed systems. The source of this nitrate can be the direct rapid leaching of nitrate from fertilizer or the export of nitrate mineralized from stored soil organic matter.

At annual time scales, we find a strong relationship between fertilizer input and the export of total nitrogen from a watershed (Figure 3c). NANI, on the contrary, is only weakly correlated to total nitrogen export Figure 3a), which is counter to observations made in other regions [17••]. The relationship between discharge and river N flux is also surprisingly weak (Figure 3b). Collectively these results demonstrate that high rates of fertilizer application provide a mobile source of nitrogen that can regulate river nitrogen concentrations and rating curves (Figure 2).

The slope of the linear regression between total nitrogen flux and fertilizer application rate indicates that ~35% of fertilizer N is exported from Mississippi-basin watersheds on an average annual basis (Figure 2c). In comparison, Howarth *et al.* [18••] reported a slope of 0.24 for a large number of watersheds in the US and Europe, indicating that watersheds of the Mississippi export a higher fraction of applied fertilizer. David *et al.* (2010) concluded that fertilizer input was significantly correlated to the fraction of area that was row-cropped and tile-drained. When considered together, these results suggest it is the high mobility of fertilizer nitrogen, not total nitrogen input, that is most important in governing the comparatively

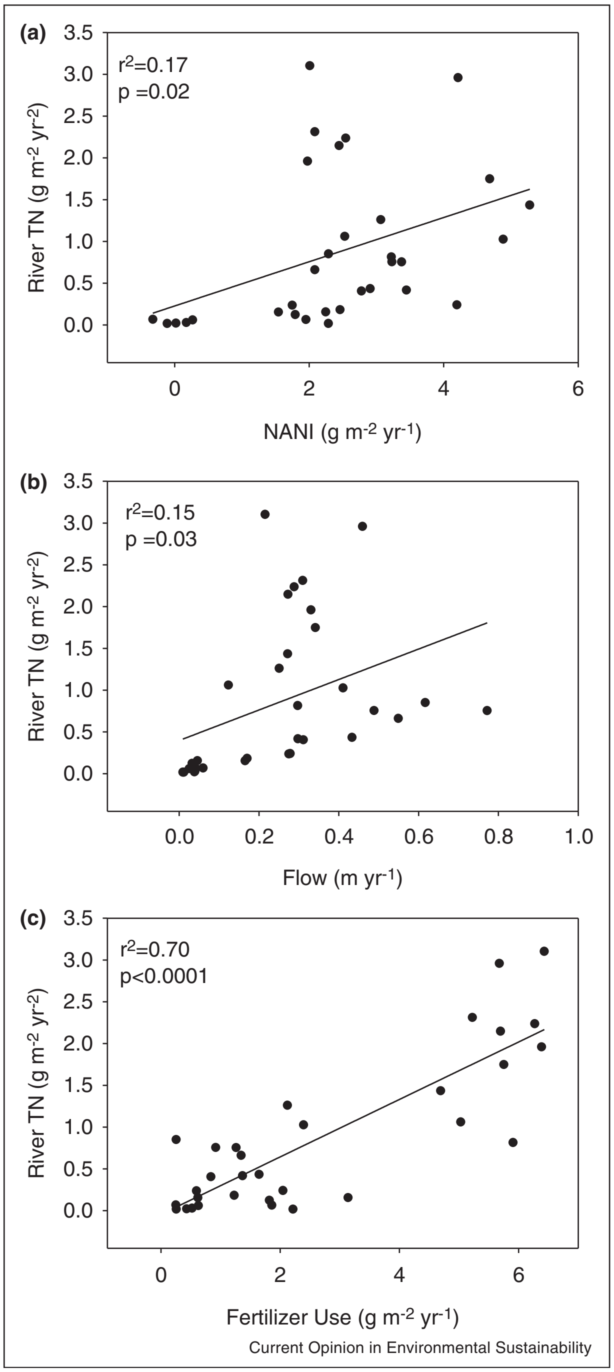
Figure 2



The relationship between fertilizer application rate and the flow weighted concentration **(a)**, the y-intercept of rating curves **(b)**, and the r^2 of the rating curves **(c)** for sub-watersheds of the Missisissippi. The relationship between the slope of the rating curve and fertilizer input was not significant ($p = 0.11$). For an example of a rating curve see Figure 1. The slope and y-intercept reported are for a linear regression of ln flow vs ln concentration. The flow weighted concentration is the average annual flow weighted concentration computed using LOADrunner (see Figure 3). The list of watersheds used in this analysis is provided in an appended table. More information on the methods is provided in the Appendix.

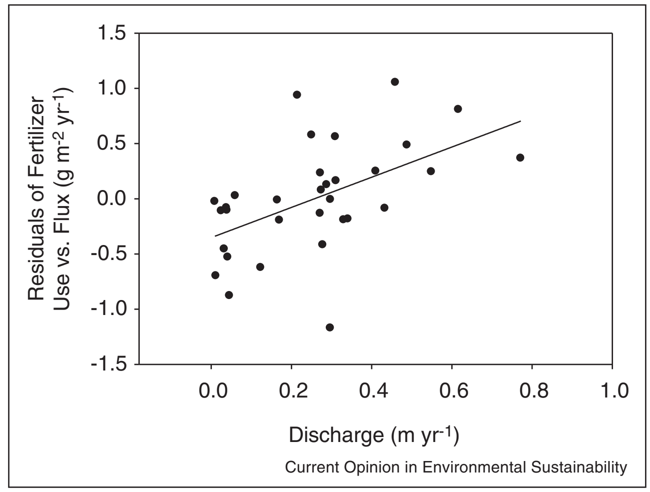
high fraction of nitrogen exported to streams and rivers that drain those watersheds of the Mississippi basin that receive high fertilizer inputs, have modified hydrology, and are intensively row-cropped.

Figure 3



The relationship between annual NANI **(a)**, flow **(b)** and fertilizer input **(c)** and River TN flux for subwatersheds of the Mississippi. See the appendix for methods. The list of watersheds used in this analysis is provided in the appended excel file and the method is discussed in more detail in the appendix. The slopes of these graphs are 0.2600, 1.8, and 0.34, for **a**, **b**, and **c** respectively. The *y*-intercepts are 0.23, 0.39, and −0.045.

Figure 4



The relationship between discharge and the residuals of the linear relationship between fertilizer input and river N flux (Figure 3**c**). The relationship has an r^2 of 0.28 and a p of 0.0020. The list of watersheds used in this analysis is provided in the appended excel file.

Interestingly, the residuals of the relationship between nitrogen export and fertilizer application can be predicted in terms of the discharge rate (Figure 4). This observation is consistent with past studies that demonstrate a higher percentage of NANI exported from wetter watersheds and during wetter years [19,20]. A multiple regression of data in the appended table leads to the following relationship:

$$\text{River N Export}(\text{g m}^{-2}\ \text{yr}^{-1}) = 0.33F + 1.38Q - 0.364(r^2 = 0.78) \quad (1)$$

where F is fertilizer application rate (g m^{-2} yr^{-1}) and Q is annual discharge (m yr^{-1}). David *et al.* (2010) similarly found that fertilizer and discharge are key predictors of nitrogen export. Eq. (1) predicts that for every additional g of fertilizer applied within a watershed, an extra 0.34 g of nitrogen (34%) will be exported, while each cm increase in discharge will cause an additional 14.1 g m^{-2} yr^{-1} of nitrogen to be exported per km^2 per year. Thus, as precipitation and discharge increase, the residence time of watershed nitrogen decreases and a greater percentage of fertilizer nitrogen is exported to the drainage network.

The influence of hydrology

The relationship between discharge and nitrogen export (Figure 4) highlights the importance of water throughput to nitrogen fluxes. The impact of hydrologic events on nutrient export from agricultural systems occurs at both the local and regional scale. At the small watershed scale, there is often an increase in the concentration of dissolved nitrogen during hydrologic events owing to changing flow paths and hydrologic connections that flush stored nitrate from soils (Figure 1 [21,22]). Even if stream-water concentrations decrease, nutrient fluxes generally increase owing to the order-of-magnitude increases in discharge during hydrologic events (Figure 1). The characteristics of the watershed-export response during hydrologic events will ultimately depend on timing and amount of nutrient loading and antecedent hydrologic conditions [8,21].

Nitrate removal within the stream network itself is also impacted by hydrologic events. Nitrate flushed from the landscape to streams and rivers during hydrologic events, when stream-water residence times are low, has little opportunity to be transformed by rate-limited reactions, particularly during spring events when temperatures are low [23•]. Furthermore, the percentage of stream-water that exchanges with the hyporheic zone – hotspots for denitrification – generally decreases with stream discharge and hence is comparatively low during hydrologic events [24,25]. The changes in stream-water residence time and hyporheic exchange that occur during hydrologic events are consistent with the observation that removal of nitrate by denitrification within agricultural streams is limited to low flow summer periods [26]. Thus, the application of nutrients as fertilizer represents a very mobile form of nutrients that can be pulsed to streams and the nutrients delivered during pulses may exceed the capacity for in-stream processing. This is critical with respect to the Gulf of Mexico response owing to the importance of spring time nitrogen fluxes to the development of hypoxia.

At the regional scale, models predict that higher discharge years lead to a greater flux of nutrients. Part of the explanation is that nitrate stored during dry years is exported during wet years [8,27,28], demonstrating an impact of watershed storage, or watershed memory, on net nitrogen dynamics. There is also a long-term effect in which watersheds with higher precipitation export a greater percentage of nitrogen inputs owing to a decrease in the processing time, or residence time, with higher water throughput. Thus in managed systems that receive high nitrogen inputs, increases in precipitation might decrease potential nitrogen flux for the following year owing to the flushing of stored nitrogen [27,28]; however, the response of a watershed to a long-term increase in precipitation is an increase in the percentage of fertilizer delivered to streams (Figure 4).

The residence time of water and nitrate in agricultural watersheds is impacted by more than precipitation amounts. Agricultural practices, such as tile drainage, can also greatly alter the delivery of nitrogen to streams. Many studies have demonstrated that tile drained systems have higher nitrate fluxes and peak runoff rates [21,29], with the two being related through reductions in watershed storage and corresponding decreases in watershed residence times. Tile drainage losses are also particular susceptible to losses during spring storms, a sensitive time period with respect to the Gulf of Mexico hypoxia [23•]. Continuous corn and corn–soybean rotations also have more limited evapotranspiration compared to agricultural systems with cover crops, which also leads to greater water throughput and nitrate losses [30]. David *et al.* (2010) reported that tile drainage could predict 17% of the spatial variation in winter-spring nitrate yield. New patterned tile drainage systems are installed every year in the upper Midwest, intensifying drainage (Richard A. Cooke, personal communication). Thus we assert that in addition to intensive fertilization, alterations of water and nitrate residence times, driven by climate and agricultural practices, are also important drivers of nutrient export to the Gulf of Mexico.

The implications of hydrologic disturbances on nitrogen fluxes are not inconsequential. Raymond *et al.* (2008) reported that discharge in the Mississippi has increased by $\sim$84 km^3 during the past century. The average decadal discharge for the 1930s–1960s is 489 ± 32 km^3, while the average discharge for the 1970–2010 is 604 ± 49 km^3. Raymond *et al.* (2008) also reported that a greater proportion of water is now originating from the agricultural lands of the Mississippi. This is consistent with other studies demonstrating an increase in discharge in the Midwest [31]. Using the long-term data from the 65 Mississippi subwatersheds described in Raymond *et al.* (2008) yields the following relationship for the change in discharge:

$$\Delta Q = 0.0031P + 0.52(\Delta P) + 0.052Ag - 0.041(r^2 = 0.70) \quad (2)$$

where ΔQ is the change in annual discharge in subwatersheds of the Mississippi during the 20th century (see Raymond *et al.*, 2008), P is watershed precipitation (m yr^{-1}), ΔP is change in precipitation during the 20th century (m yr^{-1}), and Ag is the fraction of the subwatershed in agriculture. Thus, it appears that owing to land management and climate variation there is a greater proportion of water originating from the intensively managed regions of the Mississippi. For the intensively managed watersheds, the precipitation to discharge ratio is changing, which is evidence of a decrease in water residence time. Finally, increases in discharge can also indirectly enhance the size of Gulf of Mexico hypoxia owing to strengthened stratification in the Gulf of Mexico [32••].

Impact on management options

We argue that the across-system relationships reported here and elsewhere are consistent with the concept that in highly managed and productive watersheds the export of nutrients is directly controlled by the amount added by fertilization and modulated by water residence time, with water residence time being impacted by climate and agricultural practices such as tile drainage and row cropping that co-vary with fertilizer input. A large unknown in this area is the duration of the nitrogen memory effect as it relates to sustained fertilizer application. Recent studies have argued that the focus on fertilizers is perhaps over prescribed [33] and nitrogen export from the Mississippi River basin is a stationary process [34•] owing to a long watershed memory response to nitrogen fertilization.

The heterogeneous nature of soils coupled with the importance of controlling for water throughput during studies on the response of watersheds to changes in fertilizer application rates make it difficult to generalize on the memory effect. Studies have demonstrated a 14–36% decrease in nitrate losses arising from changes in the timing of fertilizer application [8,35]. In certain cases, large immediate losses of nitrogen are documented during events following fertilization in the fall/winter [36]. A study in Indiana reported a decrease in streamwater nitrate concentrations from 28 to 8 mg L^{-1} following a change from intensively fertilized corn with chisel tillage to a corn–soybean rotation that was accompanied by a 50% decrease in fertilizer input and no-tillage [37]. A study in Iowa found a decrease in flow-weighted nitrate concentrations in a 400 ha tile-drained Iowa watershed of 16.0–11.3 mg N L^{-1}following implementation of a prescriptive late spring nitrate soil test [38]. As a part of this test, nitrogen fertilizer application was reduced 23% in the watershed, which resulted in a 30% relative reduction in nitrate concentration compared to the control watershed [38]. Underlining this general point, a recent study concluded that best management practices that exclude decreases in fertilizer application rates in tile-drained watersheds often do not successfully decrease nitrate export [39].

Modeling of tile-drained watersheds indicates that N leaching is highly responsive to water throughput and fertilizer application rate [40]. Hu *et al.* estimated that a 10–50% decrease in fertilizer application would reduce N export by 10–43% [41]. Chaplot and Saleh predicted a 22 and 50% decrease in export with a 20 and 40% decrease in fertilizer application rates, respectively [42]. The length of the memory effect for nitrogen in intensively managed agricultural systems represents a major gap in knowledge with respect to managing these systems.

In the highly managed Mississippi drainage basin, the importance of managing fertilizer application, cropping systems, and hydrology to decrease nitrogen export cannot be overstated (Figures 2 and 3c). We argue that, although there is undoubtedly a memory effect, the evidence demonstrates that a significant fraction of fertilizer input is rapidly (<24 months) transported from the landscape in average to wet years in the Mississippi. Although fertilizer input is surely part of the problem, areas of the corn-belt with high fertilizer application are characterized by other properties that enhance transport to rivers and streams. Thus it is not simply the input of nitrogen or NANI and climate, but the overall engineered system that exacerbates nitrogen export and new cropping systems need to be explored [43••,44•]. In particular, shallow root systems and short growing seasons that remove nitrogen and water for only a fraction of the year, a lack of synchronicity in fertilizer application and plant uptake, and engineered drainage systems that short-circuit rainwater and snowmelt all contribute to a rapid export of nitrogen, especially during hydrologic events that are occurring with greater frequency in the recent period of changing climate [45]. Market-based policies reinforce the large footprint of these simple monoculture cropping systems that facilitate nitrogen loss [46]. A primary management option still needs to be decreasing fertilizer application and mobility, and, with respect to the Gulf of Mexico dead zone, particularly during the spring months. Primary recommendations include not over fertilizing, applying fertilizers closer to periods of plant uptake (at planting or sidedressing instead of in the fall), planting cover crops and crops with a more temporal and spatially active rooting and transpiration system, and exploring alternative drainage approaches.

The development of strategies for managing the export of nitrogen should more carefully consider watershed hydrology. The hydrology of the nation's breadbasket appears to be in a state of change [7•,31,47], with this region receiving a greater amount of precipitation than in past periods and therefore having a greater amount of 'average' or wet years. Furthermore, field work has clearly demonstrated that tile drainage and row cropping accelerate the lateral export of nutrients, particularly nitrate [48]. The increase in nutrient fluxes is therefore partly due to agricultural alterations of watershed hydrology including an increase in baseflow [49] and peak flows [50]. Owing to higher peak flows, tile drainage can also change channel geomorphology, creating laterally confined channels that decrease stream interaction with riaparian zones. [50]. Future studies need to clearly determine the impacts of climate change and agricultural practices on watershed hydrology of the breadbasket.

The impacts of hydrologic variability on nitrogen export are becoming clear. Calculations with Eq. (2) for a fertilizer application rate of 5500 kg km^2 yr^{-1} and a discharge of 40 cm yr^{-1} reveals that a 25% reduction in the amount of fertilizer applied decreases the watershed export of nitrogen by 30%. The reduction in nitrogen export may fall from 30% to 25%, however, if discharge increases [27,51] by a mere 5 cm yr^{-1}. Therefore, in accordance with recommendations made in other studies [15], management options should target average to above-average discharge years and anticipate a potential increase in discharge and subsurface drainage in future years [52,53].

A major dilemma for reducing N fertilization is that it must be done in light of potential feedbacks to agricultural systems. In the most intensively farmed fields of the upper Midwest, the current nitrogen balance can be negative or near zero [27,51]. This presents sustainability issues, as reductions in fertilization rates may lead to reductions in soil organic N pools, as well declines in crop yields. We stress that to limit nitrate export without lowering crop production, our understanding of the relationship between crop management and N input and export needs to be taken to a higher degree of specificity, which will require additional experimental research and modeling. A more spatially intense monitoring system of both riverine outflow and NANI components coupled with more detailed information on crop management particularly tile drainage is needed.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cosust.2012.04.001.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. Cloern JE: **Our evolving conceptual model of the coastal eutrophication problem**. *Marine Ecol Prog Ser* 2001, **210**:223-253.

2. Ryther JH, Dunstan WM: **Nitrogen, phosphorus, and eutrophication in a coastal marine environment**. *Science* 1971, **171**:1008.

3. Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green PA, Holland EA *et al.*: **Nitrogen cycles: past, present, and future**. *Biogeochemistry* 2004, **70**:153-226.

4. Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K, Downing JA, Elmgren R, Caraco N, Jordan T *et al.*: **Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: natural and human influences**. *Biogeochemistry* 1996, **35**:75-139.

5. Howarth RW, Boyer EW, Pabich WJ, Galloway JN: **Nitrogen use in the United States from 1961–2000 and potential future trends**. *AMBIO* 2002, **31**:88-96.

6. Dinnes DL, Karlen DL, Jaynes DB, Kaspar TC, Hatfield JL, Colvin TS, Cambardella CA: **Nitrogen management strategies to reduce nitrate leaching in tile-drained midwestern soils**. *Agronomy J* 2002, **94**:153-171.

7. • Raymond PA, Oh NH, Turner RE, Broussard W: **Anthropogenically enhanced fluxes of water and carbon from the Mississippi River**. *Nature* 2008, **451**:449-452.
Documented an increase in anion flux from Mississsippi. The increase in flux is due to higher overall discharge but also a greater proportion of water originating from agricultural fields.

8. Randall GW, Mulla DJ: **Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural practices**. *J Environ Qual* 2001, **30**:337-344.

9. Smith SV, Swaney DP, Talaue-McManus L, Bartley JD, Sandhei PT, McLaughlin CJ, Dupra VC, Crossland CJ, Buddemeier RW, Maxwell BA *et al.*: **Humans, hydrology, and the distribution of inorganic nutrient loading to the ocean**. *Bioscience* 2003, **53**:235-245.

10. • Baulch HM, Schiff SL, Maranger R, Dillon PJ: **Nitrogen enrichment and the emission of nitrous oxide from streams**. *Global Biogeochem Cycles* 2011:25.
Demonstrated a linkage between stream nitrate and nitrous oxide concentrations. Argues for a significant flux of nitrous oxide from high nitrate drainage networks.

11. Mitsch WJ, Day JW, Gilliam JW, Groffman PM, Hey DL, Randall GW, Wang NM: **Reducing nitrogen loading to the Gulf of Mexico from the Mississippi River Basin: strategies to counter a persistent ecological problem**. *Bioscience* 2001, **51**:373-388.

12. Baker JL, Campbell KL, Johnson HP, Hanway JJ: **Nitrate, phosphorus, and sulfate in subsurface drainage water**. *J Environ Qual* 1975, **4**:406-412.

13. Goolsby DA, Battaglin WA: **Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA**. *Hydrol Processes* 2001, **15**:1209-1226.

14. Turner RE, Rabalais NN: **Changes in Mississippi River water-quality this century**. *Bioscience* 1991, **41**:140-147.

15. McIsaac GF, David MB, Gertner GZ, Goolsby DA: **Relating net nitrogen input in the Mississippi River basin to nitrate flux in the lower Mississippi River: a comparison of approaches**. *J Environ Qual* 2002, **31**:1610-1622.

16. Justic D, Rabalais NN, Turner RE: **Modeling the impacts of decadal changes in riverine nutrient fluxes on coastal eutrophication near the Mississippi River Delta**. *Ecol Model* 2002, **152**:33-46.

17. •• David MB, Drinkwater LE, McLsaac GF: **Sources of nitrate yields in the Mississippi River basin**. *J Environ Qual* 2010, **39**:1657-1667.
Reported that fertilizer N did a better job of predicting river nitrate flux than NANI. Demonstrates a linkage between tile drainage and winter/spring nitrate yield.

18. •• Howarth R, Swaney D, Billen G, Garnier J, Hong B, Humborg C, Johnes P, Morth C, Marino R: **Nitrogen fluxes from the landscape are controlled by net anthropgoenic nitrogen inputs and by climate**. *Front Ecol Environ* 2012, **10**:37-43.
Analyzed 154 watersheds to conclude that NANI can predict nitrate fluxes and a higher percentage of NANI is exported from systems with greater freshwater yields.

19. Howarth RW, Swaney DP, Boyer EW, Marino R, Jaworski N, Goodale C: **The influence of climate on average nitrogen export from large watersheds in the Northeastern United States**. *Biogeochemistry* 2006, **79**:163-186.

20. Sobota DJ, Harrison JA, Dahlgren RA: **Influences of climate, hydrology, and land use on input and export of nitrogen in California watersheds**. *Biogeochemistry* 2009, **94**:43-62.

21. Royer TV, David MB, Gentry LE: **Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: implications for reducing nutrient loading to the Mississippi River**. *Environ Sci Technol* 2006, **40**:4126-4131.

22. Keeney DR, Deluca TH: **Des-Moines river nitrate in relation to watershed agricultural practices- 1945 versus 1980's**. *J Environ Qual* 1993, **22**:267-272.

23. • Cuadra PE, Vidon P: **Storm nitrogen dynamics in tile-drain flow in the US Midwest**. *Biogeochemistry* 2011, **104**:293-308.
Large storms are very important to the losses of nitrate from tile drained agricultural systems.

24. Cirmo CP, McDonnell JJ: **Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review**. *J Hydrol* 1997, **199**:88-120.

25. Karwan DL, Saiers JE: **Influences of seasonal flow regime on the fate and transport of fine particles and a dissolved solute in a New England stream**. *Water Resour Res* 2009, **45**.

26. Royer TV, Tank JL, David MB: **Transport and fate of nitrate in headwater agricultural streams in Illinois**. *J Environ Qual* 2004, **33**:1296-1304.

27. Gentry LE, David MB, Below FE, Royer TV, McLsaac GF: **Nitrogen mass balance of a tile-drained agricultural watershed in East-Central Illinois**. *J Environ Qual* 2009, **38**:1841-1847.

28. David MB, Gentry LE, Kovacic DA, Smith KM: **Nitrogen balance in and export from an agricultural watershed**. *J Environ Qual* 1997, **26**:1038-1048.

29. Skaggs RW, Breve MA, Gilliam JW: **Hydrologic and water quality impacts of agricultural drainage**. *Crit Rev Environ Sci Technol* 1994, **24**:1-32.

30. Randall GW, Huggins DR, Russelle MP, Fuchs DJ, Nelson WW, Anderson JL: **Nitrate losses through subsurface tile drainage in Conservation Reserve Program, alfalfa, and row crop systems**. *J Environ Qual* 1997, **26**:1240-1247.

31. Lins HF, Slack JR: **Streamflow trends in the United States**. *Geophys Res Lett* 1999, **26**:227-230.

32. •• Bianchi TS, DiMarco SF, Cowan JH, Hetland RD, Chapman P, Day JW, Allison MA: **The science of hypoxia in the Northern Gulf of Mexico: a review**. *Sci Total Environ* 2010, **408**:1471-1484.

Stress the importance of understanding of the bio-physical of Gulf of Mexico to discharge events. Argue that the stronger stratification during high discharge years may be a feedback in Gulf of Mexico dead zone.

33. Krug EC, Winstanley D: **The need for comprehensive and consistent treatment of the nitrogen cycle in nitrogen cycling and mass balance studies: I. Terrestrial nitrogen cycle**. *Sci Total Environ* 2002, **293**:1-29.

34. • Basu NB, Destouni G, Jawitz JW, Thompson SE, Loukinova NV, Darracq A, Zanardo S, Yaeger M, Sivapalan M, Rinaldo A *et al.*: **Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity**. *Geophys Res Lett* 2010, **37**.

Argues that loads of nitrate in agricultural systems are dominated and can be predicted by discharge.

35. Randall GW, Vetsch JA: **Nitrate losses in subsurface drainage from a corn-soybean rotation as affected by fall and spring application of nitrogen and nitrapyrin**. *J Environ Qual* 2005, **34**:590-597.

36. Gentry LE, David MB, Smith-Starks KM, Kovacic DA: **Nitrogen fertilizer and herbicide transport from tile drained fields**. *J Environ Qual* 2000, **29**:232-240.

37. Kladivko EJ, Frankenberger JR, Jaynes DB, Meek DW, Jenkinson BJ, Fausey NR: **Nitrate leaching to subsurface drains as affected by drain spacing and changes in crop production system**. *J Environ Qual* 2004, **33**:1803-1813.

38. Jaynes DB, Dinnes DL, Meek DW, Karlen DL, Cambardella CA, Colvin TS: **Using the late spring nitrate test to reduce nitrate loss within a watershed**. *J Environ Qual* 2004, **33**:669-677.

39. Lemke AM, Kirkham KG, Lindenbaum TT, Herbert ME, Tear TH, Perry WL, Herkert JR: **Evaluating agricultural best management practices in tile-drained subwatersheds of the Mackinaw River, Illinois**. *J Environ Qual* 2011, **40**:1215-1228.

40. Li CS, Farahbakhshazad N, Jaynes DB, Dinnes DL, Salas W, McLaughlin D: **Modeling nitrate leaching with a biogeochemical model modified based on observations in a row-crop field in Iowa**. *Ecol Model* 2006, **196**:116-130.

41. Hu X, McIsaac GE, David MB, Louwers CAL: **Modeling riverine nitrate export from an East-Central Illinois watershed using SWAT**. *J Environ Qual* 2007, **36**:996-1005.

42. Chaplot V, Saleh A, Jaynes DB, Arnold J: **Predicting water, sediment and NO3-N loads under scenarios of land-use and management practices in a flat watershed**. *Water Air Soil Pollut* 2004, **154**:271-293.

43. •• Hufnagl-Eichiner S, Wolf SA, Drinkwater LE: **Assessing social-ecological coupling: agriculture and hypoxia in the Gulf of Mexico**. *Global Environ Change Human Policy Dimensions* 2011, **21**:530-539.

Argues that spending on nitrogen management in the Mississippi are not conservative and need to try to encourage alternative modes of agricultural production to be transformative.

44. • Broussard W, Turner RE: **A century of changing land-use and water-quality relationships in the continental US**. *Front Ecol Environ* 2009, **7**:302-307.

Demonstrates the impact of agricultural production on water quality in the early 20th century. Argues that increased cropland diversity and perennial plant cover are needed to overcome nitrogen problems.

45. Groisman PY, Knight RW, Karl TR, Easterling DR, Sun BM, Lawrimore JH: **Contemporary changes of the hydrological cycle over the contiguous United States: trends derived from in situ observations**. *J Hydrometeorol* 2004, **5**:64-85.

46. Jordan N, Boody G, Broussard W, Glover JD, Keeney D, McCown BH, McIsaac G, Muller M, Murray H, Neal J *et al.*: **Environment – sustainable development of the agricultural bio-economy**. *Science* 2007, **316**:1570-1571.

47. McCabe GJ, Wolock DM: **A step increase in streamflow in the conterminous United States**. *Geophys Res Lett* 2002, **29**.

48. Smith DR, Livingston SJ, Zuercher BW, Larose M, Heathman GC, Huang C: **Nutrient losses from row crop agriculture in Indiana**. *J Soil Water Conserv* 2008, **63**:396-409.

49. Schilling KE, Jha MK, Zhang YK, Gassman PW, Wolter CF: **Impact of land use and land cover change on the water balance of a large agricultural watershed: historical effects and future directions**. *Water Resour Res* 2008, **44**.

50. Magner JA, Payne GA, Steffen LJ: **Drainage effects on stream nitrate-N and hydrology in south-central Minnesota (USA)**. *Environ Monit Assess* 2004, **91**:183-198.

51. Jaynes DB, Colvin TS, Karlen DL, Cambardella CA, Meek DW: **Nitrate loss in subsurface drainage as affected by nitrogen fertilizer rate**. *J Environ Qual* 2001, **30**:1305-1314.

52. Singh R, Helmers MJ, Kaleita AL, Takle ES: **Potential impact of climate change on subsurface drainage in Iowa's subsurface drained landscapes**. *J Irrig Drain Eng-ASCE* 2009, **135**:459-466.

53. Justic D, Rabalais NN, Turner RE: **Effects of climate change on hypoxia in coastal waters: a doubled CO2 scenario for the northern Gulf of Mexico**. *Limnol Oceanogr* 1996, **41**:992-1003.